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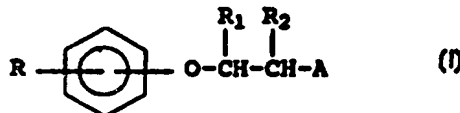
**INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)**

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<p>(21) International Application Number: <b>PCT/US97/07915</b></p> <p>(22) International Filing Date: <b>12 May 1997 (12.05.97)</b></p> <p>(30) Priority Data:              08/645,992            14 May 1996 (14.05.96)      US              08/846,717            30 April 1997 (30.04.97)      US</p> <p>(71) Applicant: <b>CHEVRON CHEMICAL COMPANY [US/US];</b>              P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p> <p>(72) Inventors: <b>CHERPECK, Richard, E.; 8962 Cypress Avenue,</b>              <b>Cotati, CA 94931 (US). MORRIS, Jack, E.; 54 Wildwood</b>              <b>Place, El Cerrito, CA 94530 (US). AHMADI, Majid, R.;</b>              <b>321 Del Monte Way, Pinole, CA 94564 (US).</b></p> <p>(74) Agents: <b>CAROLI, Claude, J. et al.; Chevron Corporation, Law</b>              <b>Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</b></p>		<p>(81) Designated States: <b>AU, BR, CA, CN, JP, KR, MX, NZ, SG,</b>              <b>European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB,</b>              <b>GR, IE, IT, LU, MC, NL, PT, SE).</b></p> <p><b>Published</b>              <i>With international search report.</i></p>

(54) Title: **FUEL ADDITIVE COMPOSITIONS CONTAINING POLYALKYPHENOXYAMINOALKANES AND POLY(OXYALKYLENE) AMINES**

(57) Abstract

A fuel additive composition comprising: (a) a polyalkylphenoxyaminoalkane having formula (I) or a fuel soluble salt thereof, wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range. The fuel additive compositions of this invention are useful as fuel additives for the prevention and control of engine deposits.



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01  
02 FUEL ADDITIVE COMPOSITIONS  
03 CONTAINING POLYALKYLPHENOXYAMINOALKANES  
04 AND POLY(OXYALKYLENE) AMINES  
05

06 BACKGROUND OF THE INVENTION  
07

08 Field of the Invention  
09

10 This invention relates to fuel additive compositions  
11 containing polyalkylphenoxyaminoalkanes and  
12 poly(oxyalkylene) amines. In a further aspect,  
13 this invention relates to the use of these additive  
14 compositions in fuel compositions to prevent and control  
15 engine deposits.  
16

17 Description of the Related Art  
18

19 It is well known that automobile engines tend to form  
20 deposits on the surface of engine components, such as  
21 carburetor ports, throttle bodies, fuel injectors, intake  
22 ports and intake valves, due to the oxidation and  
23 polymerization of hydrocarbon fuel. These deposits, even  
24 when present in relatively minor amounts, often cause  
25 noticeable driveability problems, such as stalling and poor  
26 acceleration. Moreover, engine deposits can significantly  
27 increase an automobile's fuel consumption and production of  
28 exhaust pollutants. Therefore, the development of effective  
29 fuel detergents or "deposit control" additives to prevent or  
30 control such deposits is of considerable importance and  
31 numerous such materials are known in the art.  
32

33 For example, aliphatic hydrocarbon-substituted phenols are  
34 known to reduce engine deposits when used in fuel

01 compositions. U.S. Patent No. 3,849,085, issued  
02 November 19, 1974 to Kreuz et al., discloses a motor fuel  
03 composition comprising a mixture of hydrocarbons in the  
04 gasoline boiling range containing about 0.01 to 0.25 volume  
05 percent of a high molecular weight aliphatic  
06 hydrocarbon-substituted phenol in which the aliphatic  
07 hydrocarbon radical has an average molecular weight in the  
08 range of about 500 to 3,500. This patent teaches that  
09 gasoline compositions containing minor amounts of an  
10 aliphatic hydrocarbon-substituted phenol not only prevent or  
11 inhibit the formation of intake valve and port deposits in a  
12 gasoline engine, but also enhance the performance of the  
13 fuel composition in engines designed to operate at higher  
14 operating temperatures with a minimum of decomposition and  
15 deposit formation in the manifold of the engine.  
16  
17 U.S. Patent No. 4,259,086, issued March 31, 1981 to  
18 Machleder et al., discloses a detergent additive for fuels  
19 and lubricating oils which comprises the reaction product of  
20 an aliphatic hydrocarbon-substituted phenol, epichlorohydrin  
21 and a primary or secondary monoamine or polyamine. In  
22 addition, U.S. Patent No. 4,048,081, issued September 13,  
23 1977 to Machleder et al., discloses a detergent additive for  
24 gasoline which is the reaction product of a polyisobutene  
25 phenol with epichlorohydrin, followed by amination with  
26 ethylene diamine or other polyamine.  
27  
28 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
29 1979 to Machleder et al., discloses a fuel additive  
30 composition comprising a mixture of (1) the reaction product  
31 of an aliphatic hydrocarbon-substituted phenol,  
32 epichlorohydrin and a primary or secondary mono- or  
33 polyamine, and (2) a polyalkylene phenol. This patent  
34 teaches that such compositions show excellent carburetor,

01 induction system and combustion chamber detergency and, in  
02 addition, provide effective rust inhibition when used in  
03 hydrocarbon fuels at low concentrations.

04

05 Amino phenols are also known to function as  
06 detergents/dispersants, antioxidants and anti-corrosion  
07 agents when used in fuel compositions. U.S. Patent  
08 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
09 example, discloses amino phenols having at least one  
10 substantially saturated hydrocarbon-based substituent of at  
11 least 30 carbon atoms. The amino phenols of this patent are  
12 taught to impart useful and desirable properties to  
13 oil-based lubricants and normally liquid fuels.

14

15 In addition, polybutylamines have been taught to be useful  
16 for preventing deposits in the intake system of internal  
17 combustion engines. For example, U.S. Patent No. 4,832,702,  
18 issued May 23, 1989 to Kummer et al., discloses fuel and  
19 lubricant compositions containing polybutyl or  
20 polyisobutylamine additives prepared by hydroformulating a  
21 polybutene or polyisobutene and then subjecting the  
22 resulting oxo product to a Mannich reaction or amination  
23 under hydrogenating conditions.

24

25 Polyether amine fuel additives are also well known in the  
26 art for the prevention and control of engine deposits.  
27 These polyether additives have a polyoxyalkylene "backbone",  
28 i.e., the polyether portion of the molecule consists of  
29 repeating oxyalkylene units. U.S. Patent No. 4,191,537,  
30 issued March 4, 1980 to Lewis et al., for example, discloses  
31 a fuel composition comprising a major portion of  
32 hydrocarbons boiling in the gasoline range and from 30 to  
33 2,000 ppm of a hydrocarbyl polyoxyalkylene aminocarbamate  
34 having a molecular weight from about 600 to 10,000, and at

01 least one basic nitrogen atom. The hydrocarbyl  
02 polyoxyalkylene moiety is composed of oxyalkylene units  
03 having from 2 to 5 carbon atoms in each oxyalkylene unit.  
04 These fuel compositions are taught to maintain the  
05 cleanliness of intake systems without contributing to  
06 combustion chamber deposits.

07  
08 Aromatic compounds containing a poly(oxyalkylene) moiety are  
09 also known in the art. For example, the above-mentioned U.S.  
10 Patent No. 4,191,537, discloses alkylphenyl  
11 poly(oxyalkylene) polymers which are useful as intermediates  
12 in the preparation of alkylphenyl poly(oxyalkylene)  
13 aminocarbamates.

14  
15 Similarly, U.S. Patent No. 4,881,945, issued November 21,  
16 1989 to Buckley, discloses a fuel composition comprising a  
17 hydrocarbon boiling in the gasoline or diesel range and from  
18 about 30 to about 5,000 parts per million of a fuel soluble  
19 alkylphenyl polyoxyalkylene aminocarbamate having at least  
20 one basic nitrogen and an average molecular weight of about  
21 800 to 6,000 and wherein the alkyl group contains at least  
22 40 carbon atoms.

23  
24 U.S. Patent No. 5,112,364, issued May 12, 1992 to  
25 Rath et al., discloses gasoline-engine fuels which contain  
26 small amounts of a polyetheramine and/or a polyetheramine  
27 derivative, wherein the polyetheramine is prepared by  
28 reductive amination of a phenol-initiated or alkylphenol-  
29 initiated polyether alcohol with ammonia or a primary amine.

30  
31 U.S. Patent No. 4,247,301, issued January 27, 1981 to  
32 Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene)  
33 polyamines, wherein the hydrocarbyl group contains from 1 to  
34 30 carbon atoms and the polyamine moiety contains from 2 to

01 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This  
02 patent teaches that the additives may be prepared by the  
03 reaction of a suitable hydrocarbyl-terminated polyether  
04 alcohol with a halogenating agent, such as HCl or thionyl  
05 chloride, to form a polyether chloride, followed by reaction  
06 of the polyether chloride with a polyamine to form the  
07 desired poly(oxyalkylene) polyamine. This patent also  
08 teaches at Example 6 that the polyether chloride may be  
09 reacted with ammonia or dimethylamine to form the  
10 corresponding polyether amine or polyether dimethylamine.

11

12 European Patent Application Publication No. 310,875,  
13 published April 12, 1989 discloses fuels for spark ignition  
14 engines containing a polyetheramine additive prepared by  
15 first propoxylating and/or butoxylating an alkanol or  
16 primary or secondary alkylmonoamine and then aminating the  
17 resulting polyether with ammonia or a primary aliphatic  
18 amine.

19

20 French Patent No. 2,105,539, published April 28, 1972,  
21 discloses carburetor detergent additives which are  
22 phenoxypropylamines which may be substituted with up to five  
23 hydrocarbon radicals of 1 to 30 carbon atoms on the aromatic  
24 ring. This patent also discloses additives obtained by  
25 reacting such phenoxypropylamines with alkylphosphoric  
26 acids.

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SUMMARY OF THE INVENTION

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03 It has not been discovered that the combination of certain  
04 polyalkylphenoxyaminoalkanes with poly(oxyalkylene) amines  
05 provides excellent control of engine deposits, especially  
06 intake valve deposits, when employed as fuel additives in  
07 fuel compositions.

08

09 Accordingly, the present invention provides a novel fuel  
10 additive composition comprising:

11

12 (a) A polyalkylphenoxyaminoalkane compound having the  
13 following formula or a fuel soluble salt thereof:

14

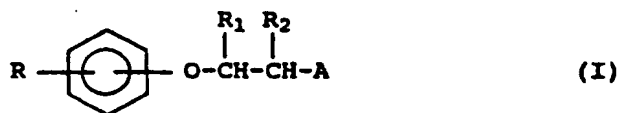
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wherein R is a polyalkyl group having an average  
molecular weight in the range of about 600 to 5,000;

R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl  
having 1 to 6 carbon atoms; and

A is amino, N-alkyl amino having about 1 to about  
20 carbon atoms in the alkyl group, N,N-dialkyl amino  
having about 1 to about 20 carbon atoms in each alkyl  
group, or a polyamine moiety having about 2 to about  
12 amine nitrogen atoms and about 2 to about 40 carbon  
atoms; and

(b) a poly(oxyalkylene) amine having at least one basic  
nitrogen atom and a sufficient number of oxyalkylene



01 units to render the poly(oxyalkylene) amine soluble in  
02 hydrocarbons boiling in the gasoline or diesel fuel  
03 range.

04  
05 The present invention further provides a fuel  
06 composition comprising a major amount of hydrocarbons  
07 boiling in the gasoline or diesel range and an  
08 effective deposit-controlling amount of the fuel  
09 additive composition of the present invention.

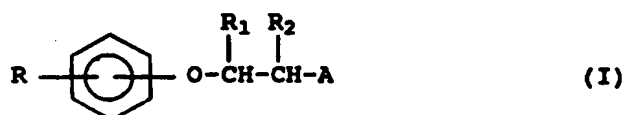
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11 The present invention additionally provides a fuel  
12 concentrate comprising an inert stable oleophilic  
13 organic solvent boiling in the range of from about  
14 150°F. to 400°F. and from about 10 to 70 weight percent  
15 of the fuel additive composition of the present  
16 invention.

17  
18 Among other factors, the present invention is based on  
19 the surprising discovery that the unique combination of  
20 certain polyalkylphenoxyaminoalkanes with  
21 poly(oxyalkylene) amines provides excellent control of  
22 engine deposits, especially on intake valves, when  
23 employed as additives in fuel compositions.

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DETAILED DESCRIPTION OF THE INVENTIONThe Polyalkylphenoxyaminoalkane

The polyalkylphenoxyaminoalkane component of the present additive composition has the general formula:



wherein R, R<sub>1</sub>, R<sub>2</sub> and A are as defined above.

Preferably, R is a polyalkyl group having an average molecular weight in the range of about 600 to 3,000, more preferably about 700 to 3,000, and most preferably about 900 to 2,500.

Preferably, one of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen. More preferably, one of R<sub>1</sub> and R<sub>2</sub> is hydrogen, methyl or ethyl, and the other is hydrogen. Most preferably, R<sub>2</sub> is hydrogen, methyl or ethyl, and R<sub>1</sub> is hydrogen.

In general, A is amino, N-alkyl amino having from about 1 to about 20 carbon atoms in the alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; N,N-dialkyl amino having from about 1 to about 20 carbon atoms in each alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; or a polyamine moiety having from about 2 to about 12 amine nitrogen atoms and from about 2 to about

01 40 carbon atoms, preferably about 2 to 12 amine nitrogen  
02 atoms and about 2 to 24 carbon atoms. More preferably, A is  
03 amino or a polyamine moiety derived from a polyalkylene  
04 polyamine, including alkylene diamine. Most preferably, A  
05 is amino or a polyamine moiety derived from ethylene diamine  
06 or diethylene triamine.

07

08 It is preferred that the R substituent is located at the  
09 meta or, more preferably, the para position on the aromatic  
10 ring, i.e., para or meta relative to the ether group.

11

12 The compounds employed in the present invention will  
13 generally have a sufficient molecular weight so as to be  
14 non-volatile at normal engine intake valve operating  
15 temperatures (about 200°-250°C.). Typically, the molecular  
16 weight of the compounds employed in this invention will  
17 range from about 700 to about 3,500, preferably from about  
18 700 to about 2,500.

19

20 Fuel-soluble salts of the compounds of formula I can be  
21 readily prepared for those compounds containing an amino or  
22 substituted amino group and such salts are contemplated to  
23 be useful for preventing or controlling engine deposits.  
24 Suitable salts include, for example, those obtained by  
25 protonating the amino moiety with a strong organic acid,  
26 such as an alkyl- or arylsulfonic acid. Preferred salts are  
27 derived from toluenesulfonic acid and methanesulfonic acid.

28

#### 29 Definitions

30

31 As used herein, the following terms have the following  
32 meanings unless expressly stated to the contrary.

33

34

- 01 The term "amino" refers to the group:  $\text{-NH}_2$ .  
02
- 03 The term "N-alkylamino" refers to the group:  $\text{-NHR}_a$  wherein  
04  $R_a$  is an alkyl group. The term "N,N-dialkylamino" refers to  
05 the group:  $\text{-NR}_b\text{R}_c$ , wherein  $R_b$  and  $R_c$  are alkyl groups.  
06
- 07 The term "hydrocarbyl" refers to an organic radical  
08 primarily composed of carbon and hydrogen which may be  
09 aliphatic, alicyclic, aromatic or combinations thereof,  
10 e.g., aralkyl or alkaryl. Such hydrocarbyl groups are  
11 generally free of aliphatic unsaturation, i.e., olefinic or  
12 acetylenic unsaturation, but may contain minor amounts of  
13 heteroatoms, such as oxygen or nitrogen, or halogens, such  
14 as chlorine.  
15
- 16 The term "alkyl" refers to both straight- and branched-chain  
17 alkyl groups.  
18
- 19 The term "lower alkyl" refers to alkyl groups having 1 to  
20 about 6 carbon atoms and includes primary, secondary and  
21 tertiary alkyl groups. Typical lower alkyl groups include,  
22 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
23 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.  
24
- 25 The term "polyalkyl" refers to an alkyl group which is  
26 generally derived from polyolefins which are polymers or  
27 copolymers of mono-olefins, particularly 1-mono-olefins,  
28 such as ethylene, propylene, butylene, and the like.  
29 Preferably, the mono-olefin employed will have 2 to about  
30 24 carbon atoms, and more preferably, about 3 to 12 carbon  
31 atoms. More preferred mono-olefins include propylene,  
32 butylene, particularly isobutylene, 1-octene and 1-decene.  
33  
34

01 Polyolefins prepared from such mono-olefins include  
02 polypropylene, polybutene, especially polyisobutene, and the  
03 polyalphaolefins produced from 1-octene and 1-decene.

04

05 The term "fuel" or "hydrocarbon fuel" refers to normally  
06 liquid hydrocarbons having boiling points in the range of  
07 gasoline and diesel fuels.

08

09 General Synthetic Procedures

10

11 The polyalkylphenoxyaminoalkanes employed in this invention  
12 may be prepared by the following general methods and  
13 procedures. It should be appreciated that where typical or  
14 preferred process conditions (e.g., reaction temperatures,  
15 times, mole ratios of reactants, solvents, pressures, etc.)  
16 are given, other process conditions may also be used unless  
17 otherwise stated. Optimum reaction conditions may vary with  
18 the particular reactants or solvents used, but such  
19 conditions can be determined by one skilled in the art by  
20 routine optimization procedures.

21

22 Those skilled in the art will also recognize that it may be  
23 necessary to block or protect certain functional groups  
24 while conducting the following synthetic procedures. In  
25 such cases, the protecting group will serve to protect the  
26 functional group from undesired reactions or to block its  
27 undesired reaction with other functional groups or with the  
28 reagents used to carry out the desired chemical  
29 transformations. The proper choice of a protecting group  
30 for a particular functional group will be readily apparent  
31 to one skilled in the art. Various protecting groups and  
32 their introduction and removal are described, for example,  
33 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*

34

01 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
02 and references cited therein.

03

04 Synthesis

05

06 The polyalkylphenoxyminoalkanes employed in the present  
07 invention may be prepared by a process which initially  
08 involves hydroxyalkylation of a polyalkylphenol of the  
09 formula:

10

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14



15 wherein R is as defined herein, with an alkylene carbonate  
16 of the formula:

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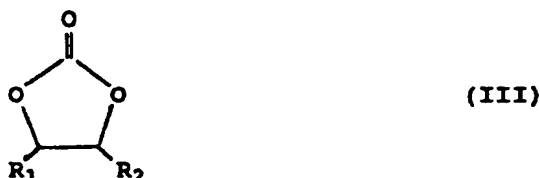
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24

25 wherein R<sub>1</sub> and R<sub>2</sub> are as defined herein, in the presence of  
26 a catalytic amount of an alkali metal hydride or hydroxide,  
27 or alkali metal salt, to provide a polyalkylphenoxyminoalkanol  
28 of the formula:

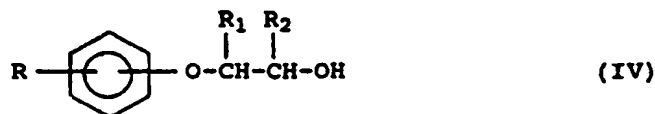
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34 wherein R, R<sub>1</sub> and R<sub>2</sub> are as defined herein.

01  
02 The polyalkylphenols of formula II are well known materials  
03 and are typically prepared by the alkylation of phenol with  
04 the desired polyolefin or chlorinated polyolefin. A further  
05 discussion of polyalkylphenols can be found, for example, in  
06 U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

07  
08 Accordingly, the polyalkylphenols of formula II may be  
09 prepared from the corresponding olefins by conventional  
10 procedures. For example, the polyalkylphenols of formula II  
11 above may be prepared by reacting the appropriate olefin or  
12 olefin mixture with phenol in the presence of an alkylating  
13 catalyst at a temperature of from about 25°C. to 150°C., and  
14 preferably 30°C. to 100°C. either neat or in an essentially  
15 inert solvent at atmospheric pressure. A preferred  
16 alkylating catalyst is boron trifluoride. Molar ratios of  
17 reactants may be used. Alternatively, molar excesses of  
18 phenol can be employed, i.e., 2 to 3 equivalents of phenol  
19 for each equivalent of olefin with unreacted phenol  
20 recycled. The latter process maximizes monoalkylphenol.  
21 Examples of inert solvents include heptane, benzene,  
22 toluene, chlorobenzene and 250 thinner which is a mixture of  
23 aromatics, paraffins and naphthenes.

24  
25 The polyalkyl substituent on the polyalkylphenols employed  
26 in the invention is generally derived from polyolefins which  
27 are polymers or copolymers of mono-olefins, particularly  
28 1-mono-olefins, such as ethylene, propylene, butylene, and  
29 the like. Preferably, the mono-olefin employed will have 2  
30 to about 24 carbon atoms, and more preferably, about 3 to  
31 12 carbon atoms. More preferred mono-olefins include  
32 propylene, butylene, particularly isobutylene, 1-octene and  
33 1-decene. Polyolefins prepared from such mono-olefins  
34 include polypropylene, polybutene, especially polyisobutene,

01 and the polyalphaolefins produced from 1-octene and  
02 1-decene.

03

04 The preferred polyisobutenes used to prepare the presently  
05 employed polyalkylphenols are polyisobutenes which comprise  
06 at least about 20% of the more reactive methylvinylidene  
07 isomer, preferably at least 50% and more preferably at least  
08 70%. Suitable polyisobutenes include those prepared using  
09  $\text{BF}_3$  catalysts. The preparation of such polyisobutenes in  
10 which the methylvinylidene isomer comprises a high  
11 percentage of the total composition is described in U.S.  
12 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,  
13 known as "reactive" polyisobutenes, yield high molecular  
14 weight alcohols in which the hydroxyl group is at or near  
15 the end of the hydrocarbon chain. Examples of suitable  
16 polyisobutenes having a high alkylvinylidene content include  
17 Ultravis 30, a polyisobutene having a number average  
18 molecular weight of about 1300 and a methylvinylidene  
19 content of about 74%, and Ultravis 10, a polyisobutene  
20 having a number average molecular weight of about 950 and a  
21 methylvinylidene content of about 76%, both available from  
22 British Petroleum.

23

24 The alkylene carbonates of formula III are known compounds  
25 which are available commercially or can be readily prepared  
26 using conventional procedures. Suitable alkylene carbonates  
27 include ethylene carbonate, propylene carbonate,  
28 1,2-butylene carbonate, 2,3-butylene carbonate, and the  
29 like. A preferred alkylene carbonate is ethylene carbonate.

30

31 The catalyst employed in the reaction of the polyalkylphenol  
32 and alkylene carbonate may be any of the well known  
33 hydroxyalkylation catalysts. Typical hydroxyalkylation  
34 catalysts include alkali metal hydrides, such as lithium



01 hydride, sodium hydride and potassium hydride, alkali metal  
02 hydroxides, such as sodium hydroxide and potassium  
03 hydroxide, and alkali metal salts, for example, alkali metal  
04 halides, such as sodium chloride and potassium chloride, and  
05 alkali metal carbonates, such as sodium carbonate and  
06 potassium carbonate. The amount of catalyst employed will  
07 generally range from about 0.01 to 1.0 equivalent,  
08 preferably from about 0.05 to 0.3 equivalent.

09

10 The polyalkylphenol and alkylene carbonate are generally  
11 reacted in essentially equivalent amounts in the presence of  
12 the hydroxyalkylation catalyst at a temperature in the range  
13 of about 100°C. to 210°C., and preferably from about 150°C.  
14 to about 170°C. The reaction may take place in the presence  
15 or absence of an inert solvent.

16

17 The time of reaction will vary depending on the particular  
18 alkylphenol and alkylene carbonate reactants, the catalyst  
19 used and the reaction temperature. Generally, the reaction  
20 time will range from about two hours to about five hours.

21 The progress of the reaction is typically monitored by the  
22 evolution of carbon dioxide. At the completion of the  
23 reaction, the polyalkylphenoxyalkanol product is isolated  
24 using conventional techniques.

25

26 The hydroxyalkylation reaction of phenols with alkylene  
27 carbonates is well known in the art and is described, for  
28 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030  
29 and 4,341,905.

30

31

32

33

34

01 Alternatively, the polyalkylphenoxyalkanol product of  
02 formula IV may be prepared by reacting the polyalkylphenol  
03 of formula II with an alkylene oxide of the formula:



10 wherein R<sub>1</sub> and R<sub>2</sub> are as defined herein, in the presence of  
11 a hydroxyalkylation catalyst as described above.  
12

13 Suitable alkylene oxides of formula V include ethylene  
14 oxide, propylene oxide, 1,2-butylen oxide, 2,3-butylen  
15 oxide, and the like. A preferred alkylene oxide is ethylene  
16 oxide.  
17

18 In a manner similar to the reaction with alkylene carbonate,  
19 the polyalkylphenol and alkylene oxide are reacted in  
20 essentially equivalent or equimolar amounts in the presence  
21 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,  
22 such as sodium or potassium hydride, at a temperature in the  
23 range of about 30°C. to about 150°C., for about 2 to about  
24 24 hours. The reaction may be conducted in the presence or  
25 absence of a substantially anhydrous inert solvent.  
26 Suitable solvents include toluene, xylene, and the like.  
27 Generally, the reaction is conducted at a pressure  
28 sufficient to contain the reactants and any solvent present,  
29 typically at atmospheric or higher pressure. Upon  
30 completion of the reaction, the polyalkylphenoxyalkanol is  
31 isolated by conventional procedures.  
32

33  
34

01 The polyalkylphenoxyalkanol of formula IV is subsequently  
02 reacted, either directly or through an intermediate, with an  
03 appropriate amine to provide the desired  
04 polyalkylphenoxyaminoalkanes of formula I. Suitable amine  
05 reactants which may be employed to form the amine component,  
06 i.e., substituent A, of the polyalkylphenoxyaminoalkanes  
07 employed in the present invention are discussed more fully  
08 below.

09

10 The Amine Component of the Polyalkylphenoxyaminoalkane

11

12 In general, the amine component of the presently employed  
13 polyalkylphenoxyaminoalkanes will contain an average of at  
14 least about one basic nitrogen atom per molecule. A "basic  
15 nitrogen atom" is one that is titratable by a strong acid,  
16 for example, a primary, secondary, or tertiary amine  
17 nitrogen; as distinguished from, for example, an carbamyl  
18 nitrogen, e.g.,  $-OC(O)NH-$ , which is not titratable with a  
19 strong acid. Preferably, at least one of the basic nitrogen  
20 atoms of the amine component will be primary or secondary  
21 amine nitrogen, more preferably, at least one will be a  
22 primary amine nitrogen.

23

24 The amine component of the polyalkylphenoxyaminoalkanes  
25 employed in this invention is preferably derived from  
26 ammonia, a primary alkyl or secondary dialkyl monoamine, or  
27 a polyamine having a terminal amino nitrogen atom.

28

29 Primary alkyl monoamines useful in preparing compounds  
30 employed in the present invention contain 1 nitrogen atom  
31 and from about 1 to about 20 carbon atoms, more preferably  
32 about 1 to 6 carbon atoms, most preferably 1 to 4 carbon  
33 atoms. Examples of suitable monoamines include  
34 *N*-methylaniline, *N*-ethylaniline, *N*-*n*-propylaniline,

01 *N*-isopropylamine, *N*-*n*-butylamine, *N*-isobutylamine,  
02 *N*-*sec*-butylamine, *N*-*tert*-butylamine, *N*-*n*-pentylamine,  
03 *N*-cyclopentylamine, *N*-*n*-hexylamine, *N*-cyclohexylamine,  
04 *N*-octylamine, *N*-decylamine, *N*-dodecylamine,  
05 *N*-octadecylamine, *N*-benzylamine, *N*-(2-phenylethyl)amine,  
06 2-aminoethanol, 3-amino-1-propanol,  
07 2-(2-aminoethoxy)ethanol, *N*-(2-methoxyethyl)amine,  
08 *N*-(2-ethoxyethyl)amine and the like. Preferred primary  
09 amines are *N*-methylamine, *N*-ethylamine and *N*-*n*-propylamine.

10  
11 The amine component of the presently employed  
12 polyalkylphenoxyaminoalkanes may also be derived from a  
13 secondary dialkyl monoamine. The alkyl groups of the  
14 secondary amine may be the same or different and will  
15 generally each contain about 1 to about 20 carbon atoms,  
16 more preferably about 1 to about 6 carbon atoms, most  
17 preferably about 1 to about 4 carbon atoms. One or both of  
18 the alkyl groups may also contain one or more oxygen atoms.

19  
20 Preferably, the alkyl groups of the secondary amine are  
21 independently selected from the group consisting of methyl,  
22 ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and  
23 2-methoxyethyl. More preferably, the alkyl groups are  
24 methyl, ethyl or propyl.

25  
26 Typical secondary amines which may be used in this invention  
27 include *N,N*-dimethylamine, *N,N*-diethylamine,  
28 *N,N*-di-*n*-propylamine, *N,N*-diisopropylamine,  
29 *N,N*-di-*n*-butylamine, *N,N*-di-*sec*-butylamine,  
30 *N,N*-di-*n*-pentylamine, *N,N*-di-*n*-hexylamine,  
31 *N,N*-dicyclohexylamine, *N,N*-dioctylamine,  
32 *N*-ethyl-*N*-methylamine, *N*-methyl-*N*-*n*-propylamine,  
33 *N*-*n*-butyl-*N*-methylamine, *N*-methyl-*N*-octylamine,  
34 *N*-ethyl-*N*-isopropylamine, *N*-ethyl-*N*-octylamine,

01 N,N-di(2-hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,  
02 N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the  
03 like. Preferred secondary amines are N,N-dimethylamine,  
04 N,N-diethylamine and N,N-di-n-propylamine.

05  
06 Cyclic secondary amines may also be employed to form the  
07 additives employed in this invention. In such cyclic  
08 compounds, the alkyl groups, when taken together, form one  
09 or more 5- or 6-membered rings containing up to about  
10 20 carbon atoms. The ring containing the amine nitrogen  
11 atom is generally saturated, but may be fused to one or more  
12 saturated or unsaturated rings. The rings may be  
13 substituted with hydrocarbyl groups of from 1 to about  
14 10 carbon atoms and may contain one or more oxygen atoms.

15  
16 Suitable cyclic secondary amines include piperidine,  
17 4-methylpiperidine, pyrrolidine, morpholine,  
18 2,6-dimethylmorpholine and the like.

19  
20 Suitable polyamines can have a straight- or branched-chain  
21 structure and may be cyclic or acyclic or combinations  
22 thereof. Generally, the amine nitrogen atoms of such  
23 polyamines will be separated from one another by at least  
24 two carbon atoms, i.e., polyamines having an amina  
25 structure are not suitable. The polyamine may also contain  
26 one or more oxygen atoms, typically present as an ether or a  
27 hydroxyl group. Polyamines having a carbon-to-nitrogen ratio  
28 of from about 1:1 to about 10:1 are particularly preferred.

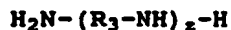
29  
30 In preparing polyalkylphenoxyaminoalkane compounds using a  
31 polyamine where the various nitrogen atoms of the polyamine  
32 are not geometrically equivalent, several substitutional  
33 isomers are possible and each of these possible isomers is  
34 encompassed within this invention.

01 A particularly preferred group of polyamines for use in the  
02 present invention are polyalkylene polyamines, including  
03 alkylene diamines. Such polyalkylene polyamines will  
04 typically contain from about 2 to about 12 nitrogen atoms  
05 and from about 2 to about 40 carbon atoms, preferably about  
06 2 to 24 carbon atoms. Preferably, the alkylene groups of  
07 such polyalkylene polyamines will contain from about 2 to  
08 about 6 carbon atoms, more preferably from about 2 to about  
09 4 carbon atoms.

10  
11 Examples of suitable polyalkylene polyamines include  
12 ethylenediamine, propylenediamine, isopropylenediamine,  
13 butylenediamine, pentylenediamine, hexylenediamine,  
14 diethylenetriamine, dipropylenetriamine,  
15 dimethylaminopropylamine, diisopropylenetriamine,  
16 dibutylenetriamine, di-sec-butylenetriamine,  
17 triethylenetetraamine, tripropylenetetraamine,  
18 triisobutylenetetraamine, tetraethylenepentamine,  
19 pentaethylenhexamine, dimethylaminopropylamine, and  
20 mixtures thereof.

21  
22 Particularly suitable polyalkylene polyamines are those  
23 having the formula:

24  
25



26  
27  
28

29 wherein  $\text{R}_3$  is a straight- or branched-chain alkylene group  
30 having from about 2 to about 6 carbon atoms, preferably from  
31 about 2 to about 4 carbon atoms, most preferably about  
32 2 carbon atoms, i.e., ethylene ( $-\text{CH}_2\text{CH}_2-$ ); and  $z$  is an  
33 integer from about 1 to about 4, preferably about 1 or  
34 about 2.

01 Particularly preferred polyalkylene polyamines are  
02 ethylenediamine, diethylenetriamine, triethylenetetraamine,  
03 and tetraethylenepentamine. Most preferred are  
04 ethylenediamine and diethylenetriamine, especially  
05 ethylenediamine.

06  
07 Also contemplated for use in the present invention are  
08 cyclic polyamines having one or more 5- to 6-membered rings.  
09 Such cyclic polyamines compounds include piperazine,  
10 2-methylpiperazine, N-(2-aminoethyl)piperazine,  
11 N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane,  
12 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the  
13 like. Among the cyclic polyamines, the piperazines are  
14 preferred.

15  
16 Many of the polyamines suitable for use in the present  
17 invention are commercially available and others may be  
18 prepared by methods which are well known in the art. For  
19 example, methods for preparing amines and their reactions  
20 are detailed in Sidgwick's "The Organic Chemistry of  
21 Nitrogen", Clarendon Press, Oxford, 1966; Noller's  
22 "Chemistry of Organic Compounds", Saunders, Philadelphia,  
23 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical  
24 Technology", 2nd Ed., especially Volume 2, pp. 99-116.

25  
26 Preparation of the Polyalkylphenoxyaminoalkane

27  
28 As noted above, the polyalkylphenoxyaminoalkanes employed in  
29 the present invention may be conveniently prepared by  
30 reacting the polyalkylphenoxyalkanol of formula IV, either  
31 directly or through an intermediate, with a nitrogen-  
32 containing compound, such as ammonia, a primary or secondary  
33 alkyl monoamine, or a polyamine, as described herein.

34

01 Accordingly, the polyalkylphenoxyalkanol of formula IV may  
02 be converted to the desired polyalkylphenoxyaminoalkane by a  
03 variety of procedures known in the art.

04

05 For example, the terminal hydroxy group on the  
06 polyalkylphenoxyalkanol may first be converted to a suitable  
07 leaving group, such as a mesylate, chloride or bromide, and  
08 the like, by reaction with a suitable reagent, such as  
09 methanesulfonyl chloride. The resulting  
10 polyalkylphenoxyalkyl mesylate or equivalent intermediate  
11 may then be converted to a phthalimide derivative by  
12 reaction with potassium phthalimide in the presence of a  
13 suitable solvent, such as *N,N*-dimethylformamide. The  
14 polyalkylphenoxyalkyl phthalimide derivative is subsequently  
15 converted to the desired polyalkylphenoxyaminoalkane by  
16 reaction with a suitable amine, such as hydrazine.  
17 Alternatively, the leaving group can be converted to an  
18 azide, as described, for example, in Turnbull Scriven,  
19 Chemical Reviews, Volume 88, pages 297-368, 1988. The azide  
20 is subsequently converted to the desired  
21 polyalkylphenoxyaminoalkane by reduction with hydrogen and a  
22 catalyst, such as palladium on carbon or a Lindlar catalyst.

23

24 The polyalkylphenoxyalkanol of formula IV may also be  
25 converted to the corresponding polyalkylphenoxyalkyl  
26 chloride by reaction with a suitable halogenating agent,  
27 such as HCl, thionyl chloride, or epichlorohydrin, followed  
28 by displacement of the chloride with a suitable amine, such  
29 as ammonia, a primary or secondary alkyl monoamine, or a  
30 polyamine, as described, for example, in U.S. Patent  
31 No. 4,247,301 to Honnen, the disclosure of which is  
32 incorporated herein by reference.

33

34



01 Alternatively, the polyalkylphenoxyaminoalkanes employed in  
02 the present invention may be prepared from the corresponding  
03 polyalkylphenoxyalkanol by a process commonly referred to as  
04 reductive amination, such as described in U.S. Patent  
05 No. 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595  
06 to Herbstman et al., the disclosures of which are  
07 incorporated herein by reference.

08  
09 In the reductive amination procedure, the  
10 polyalkylphenoxyalkanol is aminated with an appropriate  
11 amine, such as ammonia or a primary alkyl monoamine, in the  
12 presence of hydrogen and a hydrogenation-dehydrogenation  
13 catalyst. The amination reaction is typically carried out  
14 at temperatures in the range of about 160°C to about 250°C  
15 and pressures of about 1,000 to about 5,000 psig, preferably  
16 about 1,500 to about 3,000 psig. Suitable hydrogenation-  
17 dehydrogenation catalysts include those containing platinum,  
18 palladium, cobalt, nickel, copper, or chromium, or mixtures  
19 thereof. Generally, an excess of the ammonia or amine  
20 reactant is used, such as about a 5-fold to about 60-fold  
21 molar excess, and preferably about a 10-fold to about  
22 40-fold molar excess, of ammonia or amine.

23  
24 When the reductive amination is carried out with a polyamine  
25 reactant, the amination is preferably conducted using a two-  
26 step procedure as described in commonly-assigned copending  
27 U.S. Patent application Serial No. 08/574,485, filed  
28 December 19, 1995, and titled, "*Reductive Amination Process  
29 for Manufacturing a Fuel Additive From Polyoxybutylene  
30 Alcohol with Ethylene Diamine*", the disclosure of which is  
31 incorporated herein by reference in its entirety. According  
32 to this procedure, an appropriate alcohol is first contacted  
33 with a hydrogenation-dehydrogenation catalyst at a  
34 temperature of at least 230°C to provide a carbonyl-

01 containing intermediate, which is subsequently reacted with  
02 a polyamine at a temperature below about 190°C in the  
03 presence of hydrogen and a hydrogenation catalyst to produce  
04 the desired polyamine adduct.

05

06 In an alternative procedure for preparing the  
07 polyalkylphenoxyaminoalkanes employed in the present  
08 invention, the polyalkylphenol of formula II may be reacted  
09 with an aziridine of the formula:

10

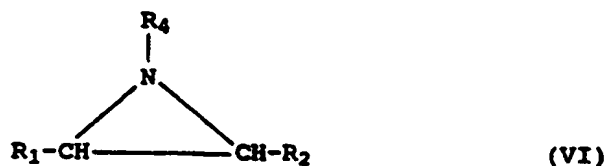
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13

14

15



16

17

18 wherein  $R_1$  and  $R_2$  are as defined herein, and  $R_4$  is hydrogen  
19 or alkyl of 1 to 20 carbon atoms. A preferred aziridine is  
20 one wherein  $R_1$  is hydrogen,  $R_2$  is hydrogen, methyl or ethyl,  
21 and  $R_4$  is hydrogen.

22

23 The reaction of aziridines with alcohols to produce beta-  
24 amino ethers is well known in the art and is discussed, for  
25 example, in Ham and Dermer, "Ethyleneimine and Other  
26 Aziridines", Academic Press, New York, 1969, pages 224-227  
27 and 256-257.

28

#### 29 The Poly(oxyalkylene) Amine

30

31 The poly(oxyalkylene) amine component of the present fuel  
32 additive composition is a poly(oxyalkylene) amine having at  
33 least one basic nitrogen atom and a sufficient number of  
34 oxyalkylene units to render the poly(oxyalkylene) amine

01 soluble in hydrocarbons boiling in the gasoline or diesel  
02 range.  
03  
04 Preferably, such poly(oxyalkylene) amines will also be of  
05 sufficient molecular weight so as to be nonvolatile at  
06 normal engine intake valve operating temperatures, which are  
07 generally in the range of about 200°C to 250°C.  
08  
09 Generally, the poly(oxyalkylene) amines suitable for use in  
10 the present invention will contain at least about  
11 5 oxyalkylene units, preferably about 5 to 100, more  
12 preferably about 8 to 100, and even more preferably about 10  
13 to 100. Especially preferred poly(oxyalkylene) amines will  
14 contain about 10 to 25 oxyalkylene units.  
15  
16 The molecular weight of the presently employed  
17 poly(oxyalkylene) amines will generally range from about 500  
18 to about 10,000, preferably from about 500 to about 5,000.  
19  
20 Suitable poly(oxyalkylene) amine compounds for use in the  
21 present invention include hydrocarbyl poly(oxyalkylene)  
22 polyamines as disclosed, for example, in U.S. Patent  
23 No. 4,247,301, issued January 27, 1981 to Honnen, the  
24 disclosure of which is incorporated herein by reference.  
25 These compounds are hydrocarbyl poly(oxyalkylene) polyamines  
26 wherein the poly(oxyalkylene) moiety comprises at least one  
27 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to  
28 5 carbon atom oxyalkylene units, and wherein the  
29 poly(oxyalkylene) chain is bonded through a terminal carbon  
30 atom to a nitrogen atom of a polyamine having from 2 to  
31 about 12 amine nitrogen atoms and from 2 to about 40 carbon  
32 atoms with a carbon-to-nitrogen ratio between about 1:1 and  
33 10:1. The hydrocarbyl group on these hydrocarbyl  
34 poly(oxyalkylene) polyamines will contain from about 1 to

01 30 carbon atoms. These compounds generally have molecular  
02 weights in the range of about 500 to 10,000, preferably from  
03 about 500 to 5,000 and more preferably from about 800 to  
04 5,000.

05  
06 The above-described hydrocarbyl poly(oxyalkylene) polyamines  
07 are prepared by conventional procedures known in the art, as  
08 taught, for example, in U.S. Patent No. 4,247,301.

09  
10 Other poly(oxyalkylene) amines suitable for use in the  
11 present invention are the poly(oxyalkylene) polyamines  
12 wherein the poly(oxyalkylene) moiety is connected to the  
13 polyamine moiety through an oxyalkylene hydroxy-type linkage  
14 derived from an epihalohydrin, such as epichlorohydrin or  
15 epibromohydrin. This type of poly(oxyalkylene) amine having  
16 an epihalohydrin-derived linkage is described, for example,  
17 in U.S. Patent No. 4,261,704, issued April 14, 1981 to  
18 Langdon, the disclosure of which is incorporated herein by  
19 reference.

20  
21 Useful polyamines for preparing the epihalohydrin-derived  
22 poly(oxyalkylene) polyamines include, for example, alkylene  
23 polyamines, polyalkylene polyamines, cyclic amines, such as  
24 piperazines, and amino-substituted amines. The  
25 poly(oxyalkylene) polyamines having an epihalohydrin-derived  
26 linkage between the poly(oxyalkylene) and polyamine moieties  
27 are prepared using known procedures as taught, for example,  
28 in U.S. Patent No. 4,261,704.

29  
30 Another type of poly(oxyalkylene) amine useful in the  
31 present invention is a highly branched alkyl  
32 poly(oxyalkylene) monoamine as described, for example in  
33 U.S. Patent No. 5,094,667, issued March 10, 1992 to  
34 Schilowitz et al., the disclosure of which is incorporated

01 herein by reference. These highly branched alkyl  
02 poly(oxyalkylene) monoamines have the general formula:

03

04

05



06

07

08 wherein  $R_4$  is a highly branched alkyl group containing from  
09 12 to 40 carbon atoms, preferably an alkyl group having  
10 20 carbon atoms which is derived from a Guerbet condensation  
11 reaction, and  $p$  is a number up to 30, preferably 4 to 8.  
12 The preferred alkyl group is derived from a Guerbet alcohol  
13 containing 20 carbon atoms having the formula:

14

15

16

17

18



19 wherein  $R_5$  is a hydrocarbyl chain.

20

21 The above highly branched alkyl poly(oxyalkylene) monoamines  
22 are prepared by using known methods as disclosed, for  
23 example, in U.S. Patent No. 5,094,667.

24

25 A preferred class of poly(oxyalkylene) amine for use in the  
26 fuel additive composition of the present invention are  
27 hydrocarbyl poly(oxyalkylene) monoamines as described, for  
28 example, in U.S. Patent No. 5,112,364, issued May 12, 1992  
29 to Rath et al., the disclosure of which is incorporated  
30 herein by reference. As disclosed in U.S. Patent  
31 No. 5,112,364, such poly(oxyalkylene) monoamines may be  
32 prepared by the reductive amination of a phenol-initiated or  
33 alkylphenol-initiated poly(oxyalkylene) alcohol with ammonia  
34 or a primary amine.

01 In addition, the above-mentioned U.S. Patent No. 4,247,301  
02 to Honnen discloses hydrocarbyl poly(oxyalkylene) monoamines  
03 which are suitable for use in the present fuel additive  
04 composition. In particular, Example 6 of this patent  
05 describes alkylphenyl poly(oxyalkylene) monoamines prepared  
06 from ammonia and dimethylamine.

07

08 A particularly preferred type of hydrocarbyl  
09 poly(oxyalkylene) monoamine is an alkylphenyl  
10 poly(oxyalkylene) monoamine wherein the poly(oxyalkylene)  
11 moiety contains oxypropylene units or oxybutylene units or  
12 mixtures of oxypropylene and oxybutylene units. Preferably,  
13 the alkyl group on the alkylphenyl moiety is a straight or  
14 branched-chain alkyl of 1 to 24 carbon atoms. An especially  
15 preferred alkylphenyl moiety is tetrapropenylphenyl, that  
16 is, where the alkyl group is a branched-chain alkyl of  
17 12 carbon atoms derived from propylene tetramer.

18

19 A further discussion of the hydrocarbon-substituted  
20 poly(oxyalkylene) moiety on the poly(oxyalkylene) amine  
21 component of the present fuel additive composition is found  
22 hereinbelow.

23

24 Another preferred class of poly(oxyalkylene) amine for use  
25 in the fuel additive composition of the present invention  
26 are hydrocarbyl-substituted poly(oxyalkylene)  
27 aminocarbamates disclosed, for example, in U.S. Patent  
28 Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930;  
29 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the  
30 disclosure of each of which are incorporated herein by  
31 reference.

32

33 These hydrocarbyl poly(oxyalkylene) aminocarbamates contain  
34 at least one basic nitrogen atom and have an average

01 molecular weight of about 500 to 10,000, preferably about  
02 500 to 5,000, and more preferably about 1,000 to 3,000. As  
03 described more fully hereinbelow, these hydrocarbyl  
04 poly(oxyalkylene) aminocarbamates contain (a) a  
05 poly(oxyalkylene) moiety, (b) an amine moiety and (c) a  
06 carbamate connecting group.

07  
08 A. The Poly(oxyalkylene) Moiety

09  
10 The hydrocarbyl-terminated poly(oxyalkylene) polymers which  
11 are utilized in preparing the hydrocarbyl poly(oxyalkylene)  
12 aminocarbamates employed in the present invention are  
13 monohydroxy compounds, e.g., alcohols, often termed  
14 monohydroxy polyethers, or polyalkylene glycol monocarbyl  
15 ethers, or "capped" poly(oxyalkylene) glycols, and are to be  
16 distinguished from the poly(oxyalkylene) glycols (diols), or  
17 polyols, which are not hydrocarbyl-terminated, i.e., are not  
18 capped. These hydrocarbyl poly(oxyalkylene) alcohols may be  
19 produced by the addition of lower alkylene oxides, such as  
20 ethylene oxide, propylene oxide, butylene oxide, etc. to a  
21 hydroxy compound,  $R_9OH$ , under polymerization conditions,  
22 wherein  $R_9$  is the hydrocarbyl group which caps the  
23 poly(oxyalkylene) chain.

24  
25 In the hydrocarbyl poly(oxyalkylene) aminocarbamates  
26 employed in the present invention, the hydrocarbyl group  $R_9$   
27 will generally contain from 1 to about 30 carbon atoms,  
28 preferably from 2 to about 20 carbon atoms and is preferably  
29 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl  
30 wherein the alkyl is a straight or branched-chain of from  
31 1 to about 24 carbon atoms. More preferably,  $R_9$  is  
32 alkylphenyl wherein the alkyl group is a branched-chain of  
33 12 carbon atoms, derived from propylene tetramer, and  
34 commonly referred to as tetrapropenyl.

01  
02 The oxyalkylene units in the poly(oxyalkylene) moiety  
03 preferably contain from 2 to about 5 carbon atoms but one or  
04 more units of a larger carbon number may also be present.  
05 Generally, each poly(oxyalkylene) polymer contains at least  
06 about 5 oxyalkylene units, preferably about 5 to about  
07 100 oxyalkylene units, more preferably about 8 to about  
08 100 units, even more preferably about 10 to 100 units, and  
09 most preferably 10 to about 25 such units. The  
10 poly(oxyalkylene) moiety of the hydrocarbyl  
11 poly(oxyalkylene) aminocarbamates employed in the present  
12 invention is more fully described and exemplified in U.S.  
13 Patent No. 4,191,537, issued March 4, 1980 to Lewis, the  
14 disclosure of which is incorporated herein by reference.  
15  
16 Although the hydrocarbyl group on the hydrocarbyl  
17 poly(oxyalkylene) moiety will preferably contain from 1 to  
18 about 30 carbon atoms, longer hydrocarbyl groups,  
19 particularly longer chain alkyl phenyl groups, may also be  
20 employed. For example, alkylphenyl poly(oxyalkylene)  
21 aminocarbamates wherein the alkyl group contains at least  
22 40 carbon atoms, as described in U.S. Patent No. 4,881,945,  
23 issued November 21, 1989 to Buckley, are also contemplated  
24 for use in the present invention. The alkyl phenyl group on  
25 the aminocarbamates of U.S. Patent No. 4,881,945 will  
26 preferably contain an alkyl group of 50 to 200 carbon atoms,  
27 and more preferably, an alkyl group of 60 to 100 carbon  
28 atoms. These longer chain alkyl groups will generally be  
29 derived from olefin polymers, such as polybutene. The  
30 disclosure of U.S. Patent No. 4,881,945 is incorporated  
31 herein by reference.  
32  
33 Also contemplated for use in the present invention are  
34 alkylphenyl poly(oxypropylene) aminocarbamates wherein the



01 alkyl group is a substantially straight-chain alkyl group  
02 of about 25 to 50 carbon atoms derived from an alpha olefin  
03 oligomer of C<sub>8</sub> to C<sub>20</sub> alpha olefins, as described in  
04 PCT International Patent Application Publication  
05 No. WO 90/07564, published July 12, 1990, the disclosure of  
06 which is incorporated herein by reference.

07

08 B. The Amine Moiety

09

10 The amine moiety of the hydrocarbyl poly(oxyalkylene)  
11 aminocarbamate is preferably derived from a polyamine having  
12 from 2 to about 12 amine nitrogen atoms and from 2 to about  
13 40 carbon atoms.

14

15 The polyamine is preferably reacted with a hydrocarbyl  
16 poly(oxyalkylene) chloroformate to produce the hydrocarbyl  
17 poly(oxyalkylene) aminocarbamate fuel additive finding use  
18 within the scope of the present invention. The  
19 chloroformate is itself derived from the hydrocarbyl  
20 poly(oxyalkylene) alcohol by reaction with phosgene.

21

22 The polyamine provides the hydrocarbyl poly(oxyalkylene)  
23 aminocarbamate with, on the average, at least about one  
24 basic nitrogen atom per carbamate molecule, i.e., a nitrogen  
25 atom titratable by strong acid. The polyamine preferably  
26 has a carbon-to-nitrogen ratio of from about 1:1 to about  
27 10:1. The polyamine may be substituted with substituents  
28 selected from hydrogen, hydrocarbyl groups of from 1 to  
29 about 10 carbon atoms, acyl groups of from 2 to about  
30 10 carbon atoms, and monoketone, monohydroxy, mononitro,  
31 monocyano, alkyl and alkoxy derivatives of hydrocarbyl  
32 groups of from 1 to 10 carbon atoms. It is preferred that  
33 at least one of the basic nitrogen atoms of the polyamine is  
34 a primary or secondary amino nitrogen. The amine moiety of

01 the hydrocarbyl poly(oxyalkylene) aminocarbamates employed  
02 in the present invention has been described and exemplified  
03 more fully in U.S. Patent No. 4,191,537.

04

05 A more preferred polyamine for use in preparing the  
06 hydrocarbyl poly(oxyalkylene) aminocarbamates finding use  
07 within the scope of the present invention is a polyalkylene  
08 polyamine, including alkylenediamine, and including  
09 substituted polyamines, e.g., alkyl and hydroxyalkyl-  
10 substituted polyalkylene polyamine. Preferably, the  
11 alkylene group contains from 2 to 6 carbon atoms, there  
12 being preferably from 2 to 3 carbon atoms between the  
13 nitrogen atoms. Examples of such polyamines include  
14 ethylenediamine, diethylenetriamine, triethylenetetramine,  
15 di(trimethylene)triamine, dipropylenetriamine,  
16 tetraethylenepentamine, etc.

17

18 Among the polyalkylene polyamines, polyethylene polyamine  
19 and polypropylene polyamine containing 2 to about 12 amine  
20 nitrogen atoms and 2 to about 24 carbon atoms are especially  
21 preferred and in particular, the lower polyalkylene  
22 polyamines, e.g., ethylenediamine, diethylenetriamine,  
23 propylenediamine, dipropylenetriamine, etc., are most  
24 preferred.

25

26 C. The Aminocarbamate Connecting Group

27

28 The hydrocarbyl poly(oxyalkylene) aminocarbamate employed as  
29 the poly(oxyalkylene) amine component of the fuel additive  
30 composition of the present invention is obtained by linking

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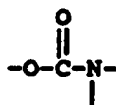
01 the polyamine and the hydrocarbyl poly(oxyalkylene) alcohol  
02 together through a carbamate linkage, i.e.,

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wherein the oxygen may be regarded as the terminal hydroxyl oxygen of the poly(oxyalkylene) alcohol, the nitrogen is derived from the polyamine and the carbonyl group  $-\text{C}(\text{O})-$ , is preferably provided by a coupling agent, such as phosgene.

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In a preferred method of preparation, the hydrocarbyl poly(oxyalkylene) alcohol is reacted with phosgene to produce a chloroformate and the chloroformate is reacted with the polyamine. Since there may be more than one nitrogen atom of the polyamine which is capable of reacting with the chloroformate, the carbamate product may contain more than one hydrocarbyl poly(oxyalkylene) moiety. It is preferred that the hydrocarbyl poly(oxyalkylene) aminocarbamate product contains on the average, about one poly(oxyalkylene) moiety per molecule (i.e., is a monocarbamate), although it is understood that this reaction route may lead to mixtures containing appreciable amounts of di- or higher poly(oxyalkylene) chain substitution on a polyamine containing several reactive nitrogen atoms.

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A particularly preferred aminocarbamate is alkylphenyl poly(oxybutylene) aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine. Synthetic methods to avoid higher degrees of substitution, methods of preparation, and other characteristics of the

01 aminocarbamates used in the present invention are more fully  
02 described and exemplified in U.S. Patent No. 4,191,537.

03

04 Fuel Compositions

05

06 The fuel additive composition of the present invention will  
07 generally be employed in hydrocarbon fuels to prevent and  
08 control engine deposits, particularly intake valve  
09 deposits. The proper concentration of additive necessary to  
10 achieve the desired deposit control varies depending upon  
11 the type of fuel employed, the type of engine, and the  
12 presence of other fuel additives.

13

14 Generally, the present fuel additive composition will be  
15 employed in a hydrocarbon fuel in a concentration ranging  
16 from about 50 to about 5,000 parts per million (ppm) by  
17 weight, preferably from 100 to 2,500 ppm.

18

19 In terms of individual components, hydrocarbon fuel  
20 containing the fuel additive composition of this invention  
21 will generally contain about 25 to 2,000 ppm of the  
22 polyalkylphenoxyaminoalkane component and about 25 to  
23 2,000 ppm of the poly(oxyalkylene) amine component. The  
24 ratio of the polyalkylphenoxyaminoalkane to  
25 poly(oxyalkylene) amine will generally range from about  
26 0.05:1 to about 5:1, and will preferably be about 2:1 or  
27 less.

28

29 The fuel additive composition of the present invention may  
30 be formulated as a concentrate using an inert stable  
31 oleophilic (i.e., dissolves in gasoline) organic solvent  
32 boiling in the range of about 150°F. to 400°F. (about 65°C.  
33 to 205°C.). Preferably, an aliphatic or an aromatic  
34 hydrocarbon solvent is used, such as benzene, toluene,

01 xylene or higher-boiling aromatics or aromatic thinners.  
02 Aliphatic alcohols containing about 3 to 8 carbon atoms,  
03 such as isopropanol, isobutylcarbinol, n-butanol and the  
04 like, in combination with hydrocarbon solvents are also  
05 suitable for use with the present additives. In the  
06 concentrate, the amount of the additive will generally range  
07 from about 10 to about 70 weight percent, preferably 10 to  
08 50 weight percent, more preferably from 20 to 40 weight  
09 percent.

10  
11 In gasoline fuels, other fuel additives may be employed with  
12 the additive composition of the present invention,  
13 including, for example, oxygenates, such as t-butyl methyl  
14 ether, antiknock agents, such as methylcyclopentadienyl  
15 manganese tricarbonyl, and other dispersants/detergents,  
16 such as hydrocarbyl amines, or succinimides. Additionally,  
17 antioxidants, metal deactivators, demulsifiers and  
18 carburetor or fuel injector detergents may be present.

19  
20 In diesel fuels, other well-known additives can be employed,  
21 such as pour point depressants, flow improvers, cetane  
22 improvers, and the like.

23  
24 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
25 used with the fuel additive composition of this invention.  
26 The carrier fluid is a chemically inert hydrocarbon-soluble  
27 liquid vehicle which substantially increases the nonvolatile  
28 residue (NVR), or solvent-free liquid fraction of the fuel  
29 additive composition while not overwhelmingly contributing  
30 to octane requirement increase. The carrier fluid may be a  
31 natural or synthetic fluid, such as mineral oil, refined  
32 petroleum oils, synthetic polyalkanes and alkenes, including  
33 hydrogenated and unhydrogenated polyalphaolefins, and  
34 synthetic polyoxyalkylene-derived fluids, such as those

01 described, for example, in U.S. Patent No. 4,191,537 to  
02 Lewis, and polyesters, such as those described, for example,  
03 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to  
04 Vogel et al., and in European Patent Application  
05 Nos. 356,726, published March 7, 1990, and 382,159,  
06 published August 16, 1990.

07  
08 These carrier fluids are believed to act as a carrier for  
09 the fuel additive composition of the present invention and  
10 to assist in removing and retarding deposits. The carrier  
11 fluid may also exhibit synergistic deposit control  
12 properties when used in combination with the fuel additive  
13 composition of this invention.

14  
15 The carrier fluids are typically employed in amounts ranging  
16 from about 25 to about 5000 ppm by weight of the hydrocarbon  
17 fuel, preferably from 100 to 3000 ppm of the fuel.  
18 Preferably, the ratio of carrier fluid to deposit control  
19 additive will range from about 0.2:1 to about 10:1, more  
20 preferably from 0.5:1 to 3:1.

21  
22 When employed in a fuel concentrate, carrier fluids will  
23 generally be present in amounts ranging from about 20 to  
24 about 60 weight percent, preferably from 30 to 50 weight  
25 percent.

#### 26 PREPARATIONS AND EXAMPLES

27  
28 A further understanding of the invention can be had in the  
29 following nonlimiting Examples. Wherein unless expressly  
30 stated to the contrary, all temperatures and temperature  
31 ranges refer to the Centigrade system and the term "ambient"  
32 or "room temperature" refers to about 20°C.-25°C. The term  
33 "percent" or "%" refers to weight percent and the term  
34 "mole" or "moles" refers to gram moles. The term

01 "equivalent" refers to a quantity of reagent equal in moles,  
02 to the moles of the preceding or succeeding reactant recited  
03 in that example in terms of finite moles or finite weight or  
04 volume. Where given, proton-magnetic resonance spectrum  
05 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are  
06 assigned as singlets (s), broad singlets (bs), doublets (d),  
07 double doublets (dd), triplets (t), double triplets (dt),  
08 quartets (q), and multiplets (m), and cps refers to cycles  
09 per second.

10

11 Example 1

12

13 Preparation of Polyisobutyl Phenol

14

15 To a flask equipped with a magnetic stirrer, reflux  
16 condenser, thermometer, addition funnel and nitrogen inlet  
17 was added 203.2 grams of phenol. The phenol was warmed to  
18 40°C. and the heat source was removed. Then,  
19 73.5 milliliters of boron trifluoride etherate was added  
20 dropwise. 1040 grams of Ultravis 10 Polyisobutene  
21 (molecular weight 950, 76% methylvinylidene, available from  
22 British Petroleum) was dissolved in 1,863 milliliters of  
23 hexane. The polyisobutene was added to the reaction at a  
24 rate to maintain the temperature between 22°C-27°C. The  
25 reaction mixture was stirred for 16 hours at room  
26 temperature. Then, 400 milliliters of concentrated ammonium  
27 hydroxide was added, followed by 2,000 milliliters of  
28 hexane. The reaction mixture was washed with water  
29 (3 X 2,000 milliliters), dried over magnesium sulfate,  
30 filtered and the solvents removed under vacuum to yield  
31 1,056.5 grams of a crude reaction product. The crude  
32 reaction product was determined to contain 80% of the

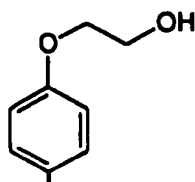
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01 desired product by proton NMR and chromatography on silica  
02 gel eluting with hexane, followed by hexane: ethylacetate:  
03 ethanol (93:5:2).

04  
05 Example 2

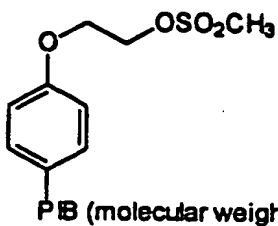
06  
07 Preparation of



15  
16  
17 Potassium hydride (1.1 grams of a 35 weight percent  
18 dispersion of in mineral oil) and 4- polyisobutyl phenol  
19 (99.7 grams, prepared as in Example 1) were added to a flask  
20 equipped with a magnetic stirrer, reflux condensor, nitrogen  
21 inlet and thermometer. The reaction was heated at 130°C for  
22 one hour and then cooled to 100°C. Ethylene carbonate  
23 (8.6 grams) was added and the mixture was heated at 160°C  
24 for 16 hours. The reaction was cooled to room temperature  
25 and one milliliter of isopropanol was added. The reaction  
26 was diluted with one liter of hexane, washed three times  
27 with water and once with brine. The organic layer was dried  
28 over anhydrous magnesium sulfate, filtered and the solvents  
29 removed *in vacuo* to yield 98.0 grams of the desired product  
30 as a yellow oil.

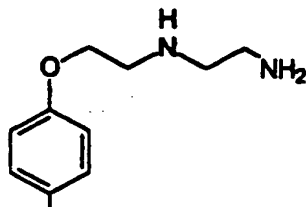
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Example 3Preparation of

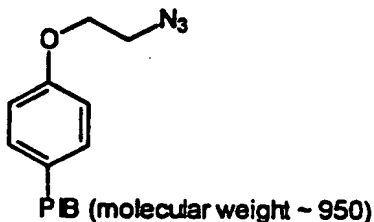
The alcohol from Example 2 (20.0 grams), triethylamine (2.9 mL), and anhydrous dichloromethane (200 mL) were combined. The solution was cooled to 0°C and methanesulfonyl chloride (1.5 mL) was added dropwise. The reaction was stirred at room temperature under nitrogen for 16 hours. The solution was diluted with dichloromethane (600 mL) and was washed twice with saturated aqueous sodium bicarbonate solution and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed *in vacuo* to yield 20.4 grams as a yellow oil.

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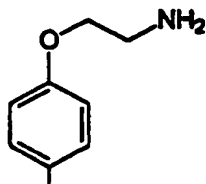
Example 4Preparation of

PIB (molecular weight ~ 950)

Ethylenediamine (12.3 mL) and anhydrous toluene (100 mL) were combined under nitrogen. The product from Example 3 (20.4 grams, dissolved in 100 mL of anhydrous toluene) was added dropwise. The resulting solution was refluxed for 16 hours. The solution was diluted with hexane (600 mL) and was washed once with saturated aqueous sodium bicarbonate solution, three times with water and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 15.1 grams as a yellow oil. The oil was chromatographed on silica gel, eluting with hexane / diethyl ether (50:50) then hexane / diethyl ether / methanol / isopropylamine (40:40:15:5) to yield 10.3 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.1 (t, 2H), 3.0 (t, 2H), 2.85 (t, 2H), 2.75 (t, 2H), 1.95 (bs, 3H), 1.5-0.7 (m, 137H).

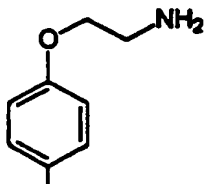
Example 5Preparation of

A mesylate prepared as described in Example 3 (406.5 grams), sodium azide (198.2 grams), Adogen 464, a methyltrialkyl (C<sub>8</sub>-C<sub>10</sub>) ammonium chloride available from Ashland Chemical (8.0 mL), N,N - dimethylformamide (800 mL) and toluene (1.2 L) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed *in vacuo*. The residue was diluted with hexane (3.0 L) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 334.3 grams of the desired azide as a yellow oil.

Example 6Preparation of

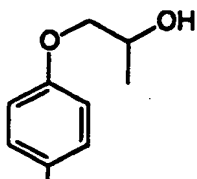
PIB (molecular weight ~ 950)

A solution of the product from Example 5 (334.3 grams) in ethyl acetate (750 mL) and toluene (750 mL), containing 10% palladium on charcoal (7.0 grams) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yielded 322.3 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.0 (t, 1H), 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

Example 6Preparation of

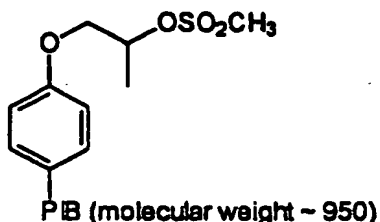
PB (molecular weight ~ 950)

A solution of the product from Example 5 (334.3 grams) in ethyl acetate (750 mL) and toluene (750 mL), containing 10% palladium on charcoal (7.0 grams) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yielded 322.3 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.0 (t, 1H), 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

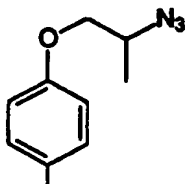
Example 7Preparation of

PIB (molecular weight ~ 950)

Potassium hydride (15.1 grams of a 35 weight percent dispersion of in mineral oil) and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 1301.7 grams of the desired product as a yellow oil.

Example 8Preparation of

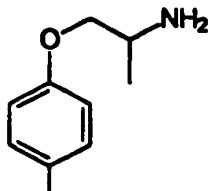
14 The alcohol from Example 7 (50.0 grams), triethylamine  
15 (7.0 mL), and anhydrous dichloromethane (500 mL) were  
16 combined. The solution was cooled to 0°C and  
17 methanesulfonyl chloride (3.7 mL) was added dropwise. The  
18 reaction was stirred at room temperature under nitrogen for  
19 16 hours. The solution was diluted with dichloromethane  
20 (1.5L) and was washed three times with saturated aqueous  
21 sodium bicarbonate solution and once with brine. The  
22 organic layer was dried over anhydrous sodium sulfate,  
23 filtered and the solvents removed in vacuo to yield  
24 57.7 grams as a yellow oil.

Example 9Preparation of

PB (molecular weight ~ 950)

The mesylate from Example 8 (57.7 grams), sodium azide (27.1 grams), Adogen 464 (1.0 mL), N,N - dimethylformamide (400 mL) and toluene (600 mL) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed in vacuo. The residue was diluted with hexane (1.5 L) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 43.1 grams of the desired azide as a yellow oil.



Example 10Preparation of

PIB (molecular weight ~ 950)

A solution of the product from Example 9 (43.1 grams) in ethyl acetate (100 mL) and toluene (100 mL), containing 10% palladium on charcoal (2.0 grams) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yielded 41.5 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.85 (d, 2H), 3.9 (abq, 1H), 3.65 (abq, 1H), 3.35 (m, 1H), 1.9 (bs, 2H), 0.7-1.6 (m, 140H).

Example 11Preparation of DodecylphenoxyPoly(oxybutylene)poly(oxypropylene) Amine

A dodecylphenoxy poly(oxybutylene) poly(oxypropylene) amine was prepared by the reductive amination with ammonia of the random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy poly(oxybutylene) poly(oxypropylene) alcohol, wherein the alcohol has an average molecular weight of about 1598. The poly(oxyalkylene) alcohol was prepared from dodecylphenol

01 using a 75/25 weight/weight ratio of butylene oxide and  
02 propylene oxide, in accordance with the procedures described  
03 in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as  
04 well as in Kirk-Othmer, "Encyclopedia of Chemical  
05 Technology", 4th edition, Volume 19, 1996, page 722. The  
06 reductive amination of the poly(oxyalkylene) alcohol was  
07 carried out using conventional techniques as described in  
08 U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

09

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### Example 12

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### Single-Cylinder Engine Test

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14 The test compounds were blended in gasoline and their  
15 deposit reducing capacity determined in an ASTM/CFR  
16 single-cylinder engine test.

17

18 A Waukesha CFR single-cylinder engine was used. Each run  
19 was carried out for 15 hours, at the end of which time the  
20 intake valve was removed, washed with hexane and weighed.  
21 The previously determined weight of the clean valve was  
22 subtracted from the weight of the valve at the end of the  
23 run. The differences between the two weights is the weight  
24 of the deposit. A lesser amount of deposit indicates a  
25 superior additive. The operating conditions of the test  
26 were as follows: water jacket temperature 200°F; intake  
27 manifold vacuum of 12 in. Hg, air-fuel ratio of 12, ignition  
28 spark timing of 40° BTC; engine speed is 1800 rpm; the  
29 engine oil is a commercial SAE 30 grade.

30

31 The amount of carbonaceous deposit in milligrams on the  
32 intake valves is reported for each of the test compounds in  
33 Table I and Table II.

34

TABLE I

Intake Valve Deposit Weight (in milligrams)			
Sample <sup>1</sup>	Run 1	Run 2	Average
Base Fuel	333.5	354.9	344.2
Example 4	22.5	22.7	22.6

<sup>1</sup>At 150 parts per million actives (ppma).

TABLE II

Intake Valve Deposit Weight (in milligrams)			
Sample <sup>1</sup>	Run 1	Run 2	Average
Base Fuel	323.8	312.1	318.0
Example 6	12.1	21.0	16.6

<sup>1</sup>At 125 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give the concentrations indicated in the tables.

The data in Table I and Table II illustrates the significant reduction in intake valve deposits provided by the polyalkylphenoxyaminoalkanes employed in the present invention (Examples 4 and 6) compared to the base fuel.

01 The combination of polyalkylphenoxylaminoalkane and  
 02 poly(oxyalkylene) amine was also tested in the single-  
 03 cylinder engine test and the amount of carbonaceous deposit  
 04 in milligrams on the intake valves is reported in Table III.

TABLE III

Sample	Conc. (ppma)	Intake Valve Deposit Weight (in milligrams)		
		Run 1	Run 2	Average
Base Fuel	-	250.3	253.1	251.6
Polyalkylphenoxy- aminoalkane/ Carrier Fluid <sup>1</sup>	50/50	188	149.8	169
Polyalkylphenoxy- aminoalkane/Poly (oxyalkylene) Amine <sup>2</sup>	50/50	9.4	4.1	6.75
Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine <sup>3</sup>	50/50	21.2	14.3	17.8
Polyalkylphenoxy- aminoalkane/ Carrier Fluid <sup>4</sup>	50/50	131.8	111.5	121.6
Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine <sup>5</sup>	50/50	0	0	0
Polyalkylphenoxy- aminoalkane/ Poly (oxyalkylene) Amine <sup>6</sup>	50/50	1	1.2	1.1

01 <sup>1</sup>Mixture of 50 ppma of polyisobutylphenoxylaminoalkane  
 02 prepared as described in Example 10 and 50 ppm of a  
 03 dodecylphenyl poly(oxybutylene) alcohol carrier fluid.

- 01 <sup>2</sup>Mixture of 50 ppma of polyisobutylphenoxyaminoalkane  
02 prepared as described in Example 10 and 50 ppma of  
03 dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine  
prepared as described in Example 11.
- 04 <sup>3</sup>Mixture of 50 ppma of polyisobutylphenoxyaminoalkane  
05 prepared as described in Example 10 and 50 ppma of a  
06 dodecylphenyl poly(oxybutylene) ethylene diamine carbamate  
07 (molecular weight about 1600), prepared essentially as  
described in Examples 6-8 of U.S. Patent No. 4,197,537.
- 08 <sup>4</sup>Mixture of 50 ppma of polyisobutylphenoxyaminoalkane  
09 prepared as described in Example 6 and 50 ppm of a  
10 dodecylphenylpoly(oxybutylene) alcohol carrier fluid.
- 11 <sup>5</sup>Mixture of 50 ppma of polyisobutylphenoxyaminoalkane  
12 prepared as described in Example 6 and 50 ppma of  
13 dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine  
prepared as described in Example 11.
- 14 <sup>6</sup>Mixture of 50 ppma of polyisobutylphenoxyaminoalkane  
15 prepared as described in Example 6 and 50 ppma of a  
16 dodecylphenyl poly(oxybutylene) ethylene diamine carbamate  
17 (molecular weight about 1600), prepared essentially as  
described in Examples 6-8 of U.S. Patent No. 4,197,537.
- 18
- 19
- 20 The data in Table III demonstrates that the combination of a  
21 polyalkylphenoxyaminoalkane and a poly(oxyalkylene) amine  
22 has a beneficial effect and gives significantly better  
23 intake valve deposit control than the  
24 polyalkylphenoxyaminoalkane component with a carrier fluid.
- 25
- 26
- 27
- 28
- 29
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01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) a polyalkylphenoxyaminoalkane compound of the  
06 formula:

07

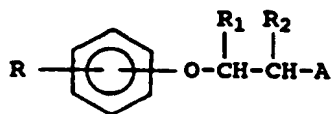
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or a fuel-soluble salt thereof, wherein R is a  
polyalkyl group having an average molecular weight  
in the range of about 600 to 5,000;

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R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower  
alkyl having 1 to 6 carbon atoms; and

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A is amino, N-alkyl amino having about 1 to about  
20 carbon atoms in the alkyl group, N,N-dialkyl  
amino having about 1 to about 20 carbon atoms in  
each alkyl group, or a polyamine moiety having  
about 2 to about 12 amine nitrogen atoms and about  
2 to about 40 carbon atoms; and

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(b) a poly(oxyalkylene) amine having at least one  
basic nitrogen atom and a sufficient number of  
oxyalkylene units to render the poly(oxyalkylene)  
amine soluble in hydrocarbons boiling in the  
gasoline or diesel fuel range.

- 01 2. The fuel additive composition according to Claim 1,  
02 wherein one of  $R_1$  and  $R_2$  is hydrogen or lower alkyl of  
03 1 to 4 carbon atoms, and the other is hydrogen.
- 04 3. The fuel additive composition according to Claim 2,  
05 wherein one of  $R_1$  and  $R_2$  is hydrogen, methyl or ethyl,  
06 and the other is hydrogen.
- 07
- 08 4. The fuel additive composition according to Claim 3,  
09 wherein  $R_2$  is hydrogen, methyl or ethyl, and  $R_1$  is  
10 hydrogen.
- 11
- 12 5. The fuel additive composition according to Claim 1,  
13 wherein R is a polyalkyl group having an average  
14 molecular weight in the range of about 600 to 3,000.
- 15 6. The fuel additive composition according to Claim 5,  
16 wherein R is a polyalkyl group having an average  
17 molecular weight in the range of about 700 to 3,000.
- 18
- 19 7. The fuel additive composition according to Claim 6,  
20 wherein R is a polyalkyl group having an average  
21 molecular weight in the range of about 900 to 2,500.
- 22
- 23 8. The fuel additive composition according to Claim 1,  
24 wherein R is a polyalkyl group derived from  
25 polypropylene, polybutene, or a polyalphaolefin  
26 oligomer of 1-octene or 1-decene.
- 27 9. The fuel additive composition according to Claim 8,  
28 wherein R is a polyalkyl group derived from  
29 polyisobutene.
- 30
- 31
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- 34

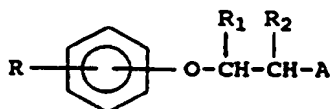
- 01 10. The fuel additive composition according to Claim 9,  
02 wherein the polyisobutene contains at least about 20%  
03 of a methylvinylidene isomer.
- 04 11. The fuel additive composition according to Claim 1,  
05 wherein A is amino, N-alkyl amino or a polyamine  
06 moiety.
- 07
- 08 12. The fuel additive composition according to Claim 11,  
09 wherein A is amino or N-alkyl amino having from about 1  
10 to about 4 carbon atoms in the alkyl group.
- 11
- 12 13. The fuel additive composition according to Claim 12,  
13 wherein A is amino.
- 14
- 15 14. The fuel additive composition according to Claim 11,  
16 wherein A is a polyamine moiety having from about 2 to  
17 about 12 amine nitrogen atoms and from about 2 to about  
18 40 carbon atoms.
- 19 15. The fuel additive composition according to Claim 14,  
20 wherein A is a polyamine moiety derived from a  
21 polyalkylene polyamine containing from about 2 to about  
22 12 amine nitrogen polyamine atoms and from about 2 to  
23 about 24 carbon atoms.
- 24
- 25 16. The fuel additive composition according to Claim 15,  
26 wherein the polyalkylene polyamine has the formula:  
27  
28
- 29 
$$\text{H}_2\text{N}-(\text{R}_3-\text{NH})_z-\text{H}$$
- 30
- 31 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
32 about 6 carbon atoms and  $z$  is an integer from about 1  
33 to about 4.
- 34



- 01 17. The fuel additive composition according to Claim 16,  
02 wherein  $R_3$  is an alkylene group having from about 2 to  
03 about 4 carbon atoms.
- 04 18. The fuel additive composition according to Claim 17,  
05 wherein the polyalkylene polyamine is ethylene diamine  
06 or diethylene triamine.  
07
- 08 19. The fuel additive composition according to Claim 18,  
09 wherein the polyalkylene polyamine is ethylene diamine.  
10
- 11 20. The fuel additive composition according to Claim 1,  
12 wherein R is a polyalkyl group derived from  
13 polyisobutene,  $R_1$  and  $R_2$  are hydrogen and A is amino or  
14 a polyamine moiety derived from ethylene diamine.  
15
- 16 21. The fuel additive composition according to Claim 1,  
17 wherein said poly(oxyalkylene) amine has a molecular  
18 weight in the range of about 500 to about 10,000.
- 19 22. The fuel additive composition according to Claim 1,  
20 wherein said poly(oxyalkylene) amine contains at least  
21 about 5 oxyalkylene units.  
22
- 23 23. The fuel additive composition according to Claim 1,  
24 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
25 poly(oxyalkylene) polyamine.
- 26 24. The fuel additive composition according to Claim 1,  
27 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
28 poly(oxyalkylene) aminocarbamate.  
29
- 30 25. The fuel additive composition according to Claim 24,  
31 wherein the hydrocarbyl group of said hydrocarbyl  
32 poly(oxyalkylene) aminocarbamate contains from 1 to  
33 about 30 carbon atoms.  
34

- 01 26. The fuel additive composition according to Claim 25,  
02 wherein said hydrocarbyl group of said hydrocarbyl  
03 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
04 group.
- 05 27. The fuel additive composition according to Claim 26,  
06 wherein the alkyl moiety of said alkylphenyl group is  
07 tetrapropenyl.  
08
- 09 28. The fuel additive composition according to Claim 24,  
10 wherein the amine moiety of said hydrocarbyl  
11 poly(oxyalkylene) aminocarbamate is derived from a  
12 polyamine having from 2 to 12 amine nitrogen atoms and  
13 from 2 to 40 carbon atoms.  
14
- 15 29. The fuel additive composition according to Claim 28,  
16 wherein said polyamine is a polyalkylene polyamine  
17 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon  
18 atoms.
- 19 30. The fuel additive composition according to Claim 29,  
20 wherein said polyalkylene polyamine is selected from  
21 the group consisting of ethylenediamine,  
22 propylenediamine, diethylenetriamine and  
23 dipropylenetriamine.  
24
- 25 31. The fuel additive composition according to Claim 24,  
26 wherein the poly(oxyalkylene) moiety of said  
27 hydrocarbyl poly(oxyalkylene) aminocarbamate is derived  
28 from C<sub>2</sub> to C<sub>5</sub> oxyalkylene units.  
29
- 30 32. The fuel additive composition according to Claim 24,  
31 wherein said hydrocarbyl poly(oxyalkylene)  
32 aminocarbamate is an alkylphenyl poly(oxybutylene)  
33 aminocarbamate, wherein the amine moiety is derived  
34 from ethylenediamine or diethylenetriamine.

- 01 33. The fuel additive composition according to Claim 1,  
02 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
03 poly(oxyalkylene) monoamine.
- 04 34. The fuel additive composition according to Claim 33,  
05 wherein said hydrocarbyl poly(oxyalkylene) monoamine is  
06 an alkylphenyl poly(oxyalkylene) monoamine, wherein the  
07 poly(oxyalkylene) moiety contains oxypropylene units or  
08 oxybutylene units or mixtures thereof.
- 09 35. The fuel additive composition according to Claim 34,  
10 wherein the alkylphenyl group is tetrapropenylphenyl.
- 11 36. A fuel composition comprising a major amount of  
12 hydrocarbons boiling in the gasoline or diesel range  
13 and an effective deposit-controlling amount of a fuel  
14 additive composition comprising:  
15  
16 (a) a polyalkylphenoxiaminoalkane compound  
17 of the formula:  
18  
19  
20  
21



27 or a fuel-soluble salt thereof, wherein R is a  
28 polyalkyl group having an average molecular weight  
29 in the range of about 600 to 5,000;

30 R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower  
31 alkyl having 1 to 6 carbon atoms; and  
32  
33  
34

- 01           A is amino, N-alkyl amino having about 1 to about  
02           20 carbon atoms in the alkyl group, N,N-dialkyl  
03           amino having about 1 to about 20 carbon atoms in  
04           each alkyl group, or a polyamine moiety having  
05           about 2 to about 12 amine nitrogen atoms and about  
06           2 to about 40 carbon atoms; and  
07  
08           (b) a poly(oxyalkylene) amine having at least one  
09           basic nitrogen atom and a sufficient number of  
10           oxyalkylene units to render the poly(oxyalkylene)  
11           amine soluble in hydrocarbons boiling in the  
12           gasoline or diesel fuel range.  
13  
14       37. The fuel composition according to Claim 36, wherein one  
15       of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1 to  
16       4 carbon atoms, and the other is hydrogen.  
17  
18       38. The fuel composition according to Claim 37, wherein R<sub>2</sub>  
19       is hydrogen, methyl or ethyl, and R<sub>1</sub> is hydrogen.  
20  
21       39. The fuel composition according to Claim 36, wherein R  
22       is a polyalkyl group having an average molecular weight  
23       in the range of about 700 to 3,000.  
24  
25       40. The fuel composition according to Claim 36, wherein R  
26       is a polyalkyl group derived from polypropylene,  
27       polybutene, or a polyalphaolefin oligomer of 1-octene  
28       or 1-decene.  
29  
30       41. The fuel composition according to Claim 40, wherein R  
31       is a polyalkyl group derived from polyisobutene.  
32  
33       42. The fuel composition according to Claim 36, wherein A  
34       is amino, N-alkyl amino or a polyamine moiety.

- 01 43. The fuel composition according to Claim 42, wherein A  
02 is amino.
- 03 44. The fuel composition according to Claim 42, wherein A  
04 is a polyamine moiety derived from a polyalkylene  
05 polyamine containing from about 2 to about 12 amine  
06 nitrogen polyamine atoms and from about 2 to about  
07 24 carbon atoms.  
08
- 09 45. The fuel composition according to Claim 44, wherein the  
10 polyalkylene polyamine has the formula:  
11  
12  
13 
$$\text{H}_2\text{N}-(\text{R}_3\text{-NH})_z\text{-H}$$
  
14
- 15 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
16 about 6 carbon atoms and  $z$  is an integer from about 1  
17 to about 4.
- 18
- 19 46. The fuel composition according to Claim 45, wherein the  
20 polyalkylene polyamine is ethylene diamine or  
21 diethylene triamine.
- 22 47. The fuel composition according to Claim 36, wherein R  
23 is a polyalkyl group derived from polyisobutene,  $\text{R}_1$  and  
24  $\text{R}_2$  are hydrogen and A is amino or a polyamine moiety  
25 derived from ethylene diamine.  
26
- 27 48. The fuel composition according to Claim 36, wherein  
28 said poly(oxyalkylene) amine is a hydrocarbyl  
29 poly(oxyalkylene) aminocarbamate.  
30
- 31 49. The fuel composition according to Claim 48, wherein the  
32 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
33 aminocarbamate contains from 1 to about 30 carbon  
34 atoms; and wherein the amine moiety of said hydrocarbyl

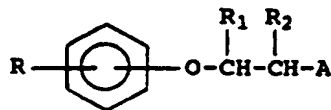
- 01 poly(oxyalkylene) aminocarbamate is derived from a  
02 polyamine having from 2 to 12 amine nitrogen atoms and  
03 from 2 to 40 carbon atoms.
- 04 50. The fuel composition according to Claim 49, wherein  
05 said hydrocarbyl group of said hydrocarbyl  
06 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
07 group; and wherein said polyalkylene polyamine is  
08 selected from the group consisting of ethylenediamine,  
09 propylenediamine, diethylenetriamine and  
10 dipropylenetriamine.  
11
- 12 51. The fuel composition according to Claim 50, wherein the  
13 alkyl moiety of said alkylphenyl group is  
14 tetrapropenyl.  
15
- 16 52. The fuel composition according to Claim 48, wherein  
17 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an  
18 alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
19 the amine moiety is derived from ethylenediamine or  
20 diethylenetriamine.
- 21 53. The fuel composition according to Claim 36, wherein  
22 said poly(oxyalkylene) amine is a hydrocarbyl  
23 poly(oxyalkylene) monoamine.  
24
- 25 54. The fuel composition according to Claim 53, wherein  
26 said hydrocarbyl poly(oxyalkylene) monoamine is an  
27 alkylphenyl poly(oxyalkylene) monoamine, wherein the  
28 poly(oxyalkylene) moiety contains oxypropylene units or  
29 oxybutylene units or mixtures thereof.  
30
- 31 55. The fuel composition according to Claim 54, wherein the  
32 alkylphenyl group is tetrapropenylphenyl.  
33  
34

01  
02  
03 56. The fuel composition according to Claim 36, wherein the  
04 composition contains from about 25 to about 2,000 parts  
05 per million by weight of said  
06 polyalkylphenoxyaminoalkane compound and about 25 to  
07 about 2,000 parts per million of said poly(oxyalkylene)  
08 amine.

09 57. The fuel composition according to Claim 36, where the  
10 composition further contains from about 25 to about  
11 5,000 parts per million by weight of a fuel-soluble,  
12 nonvolatile carrier fluid.  
13

14 58. A fuel concentrate comprising an inert stable  
15 oleophilic organic solvent boiling in the range of from  
16 about 150°F. to 400°F. and from about 10 to about  
17 70 weight percent of a fuel additive composition  
18 comprising:  
19

20 (a) a polyalkylphenoxyaminoalkane compound of the  
21 formula:  
22



29 or a fuel-soluble salt thereof, wherein R is a  
30 polyalkyl group having an average molecular weight  
31 in the range of about 600 to 5,000;  
32

33 R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower  
34 alkyl having 1 to 6 carbon atoms; and

- 01           A is amino, N-alkyl amino having about 1 to about  
02           20 carbon atoms in the alkyl group, N,N-dialkyl  
03           amino having about 1 to about 20 carbon atoms in  
04           each alkyl group, or a polyamine moiety having  
05           about 2 to about 12 amine nitrogen atoms and about  
06           2 to about 40 carbon atoms; and  
07  
08           (b) a poly(oxyalkylene) amine having at least one  
09           basic nitrogen atom and a sufficient number of  
10           oxyalkylene units to render the poly(oxyalkylene)  
11           amine soluble in hydrocarbons boiling in the  
12           gasoline or diesel fuel range.  
13  
14   59.   The fuel concentrate according to Claim 58, wherein one  
15           of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1 to  
16           4 carbon atoms, and the other is hydrogen.  
17  
18   60.   The fuel concentrate according to Claim 59, wherein R<sub>2</sub>  
19           is hydrogen, methyl or ethyl, and R<sub>1</sub> is hydrogen.  
20  
21   61.   The fuel concentrate according to Claim 58, wherein R  
22           is a polyalkyl group having an average molecular weight  
23           in the range of about 700 to 3,000.  
24  
25   62.   The fuel concentrate according to Claim 58, wherein R  
26           is a polyalkyl group derived from polypropylene,  
27           polybutene, or a polyalphaolefin oligomer of 1-octene  
28           or 1-decene.  
29  
30   63.   The fuel concentrate according to Claim 62, wherein R  
31           is a polyalkyl group derived from polyisobutene.  
32  
33   64.   The fuel concentrate according to Claim 58, wherein A  
34           is amino, N-alkyl amino or a polyamine moiety.



- 01 65. The fuel concentrate according to Claim 64, wherein A  
02 is amino.
- 03 66. The fuel concentrate according to Claim 64, wherein A  
04 is a polyamine moiety derived from a polyalkylene  
05 polyamine containing from about 2 to about 12 amine  
06 nitrogen polyamine atoms and from about 2 to about  
07 24 carbon atoms.
- 08
- 09 67. The fuel concentrate according to Claim 66, wherein the  
10 polyalkylene polyamine has the formula:  
11  
12  
13 
$$\text{H}_2\text{N}-(\text{R}_3-\text{NH})_z-\text{H}$$
  
14  
15 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
16 about 6 carbon atoms and  $z$  is an integer from about 1  
17 to about 4.
- 18
- 19 68. The fuel concentrate according to Claim 67, wherein the  
20 polyalkylene polyamine is ethylene diamine or  
21 diethylene triamine.
- 22
- 23 69. The fuel concentrate according to Claim 58, wherein R  
24 is a polyalkyl group derived from polyisobutene,  $\text{R}_1$  and  
25  $\text{R}_2$  are hydrogen and A is amino or a polyamine moiety  
26 derived from ethylene diamine.
- 27 70. The fuel concentrate according to Claim 58, wherein the  
28 fuel concentrate further contains from about 20 to  
29 about 60 weight percent of a fuel-soluble, nonvolatile  
30 carrier fluid.
- 31
- 32 71. The fuel concentrate according to Claim 58, wherein  
33 said poly(oxyalkylene) amine is a hydrocarbyl  
34 poly(oxyalkylene) aminocarbamate.

- 01 72. The fuel concentrate according to Claim 71, wherein the  
02 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
03 aminocarbamate contains from 1 to about 30 carbon  
04 atoms; and wherein the amine moiety of said hydrocarbyl  
05 poly(oxyalkylene) aminocarbamate is derived from a  
06 polyamine having from 2 to 12 amine nitrogen atoms and  
07 from 2 to 40 carbon atoms.
- 08 73. The fuel concentrate according to Claim 72, wherein  
09 said hydrocarbyl group of said hydrocarbyl  
10 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
11 group; and wherein said polyalkylene polyamine is  
12 selected from the group consisting of ethylenediamine,  
13 propylenediamine, diethylenetriamine and  
14 dipropylenetriamine.  
15
- 16 74. The fuel concentrate according to Claim 73, wherein the  
17 alkyl moiety of said alkylphenyl group is  
18 tetrapropenyl.  
19
- 20 75. The fuel concentrate according to Claim 71, wherein  
21 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an  
22 alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
23 the amine moiety is derived from ethylenediamine or  
24 diethylenetriamine.
- 25 76. The fuel concentrate according to Claim 58, wherein  
26 said poly(oxyalkylene) amine is a hydrocarbyl  
27 poly(oxyalkylene) monoamine.  
28
- 29 77. The fuel concentrate according to Claim 76, wherein  
30 said hydrocarbyl poly(oxyalkylene) monoamine is an  
31 alkylphenyl poly(oxyalkylene) monoamine, wherein the  
32 poly(oxyalkylene) moiety contains oxypropylene units or  
33 oxybutylene units or mixtures thereof.  
34

01 78. The fuel concentrate according to Claim 77, wherein the  
02 alkylphenyl group is tetrapropenylphenyl.  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/07915

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C10L 1/22

US CL : 044/424, 425, 432, 433, 434

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/424, 425, 432, 433, 434

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS search terms: polyoxyalkylene amine, fuel, 7phenoxyaminoalkane**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,366,517 A (CHERPECK) 22 November 1994, col. 2, lines 20-54.	1, 21-36, 48-58, 71-78
A	US 5,300,701 A (CHERPECK) 05 April 1994, col. 2, lines 10-33.	1-78
Y	US 5,094,667 A (SCHILOWITZ et al) 10 March 1992, col. 1, lines 32-61.	1, 21, 22, 33, 36, 53, 58, 76
Y	US 4,964,879 A (HERBSTMAN et al) 23 October 1990, col. 2, lines 3-31.	1, 21, 22, 33, 36, 53, 58, 76
Y	US 4,778,481 A (COURTNEY) 18 October 1988, col. 2, lines 7-51.	1, 21-32, 36, 48-52, 58, 71-75

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later documents published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X	documents of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* T earlier documents published on or after the international filing date	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* documents which may throw doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special cases (as specified)	* A*	document member of the same patent family
* O* documents referring to an oral disclosure, use, exhibition or other means		
* P* documents published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

27 JUNE 1997

Date of mailing of the international search report

24 JUL 1997

Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/07915

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,609,377 A (SUNG et al) 02 September 1986, col.1, lines 28-44.	1, 21, 22, 33-36, 53-55, 58, 76-78
A	US 4,604,103 A (CAMPBELL) 05 August 1986, col. 5, lines 31-51.	1-78
A	US 4,332,595 A (HERBSTMAN et al) 01 June 1982, col. 1, lines 63 to col. 2, line 9.	1-78
A	US 4,322,220 A (MACHLEDER et al) 30 March 1982, col. 2, lines 20-34 and col. 17, lines 55-65.	1-78
A	US 4,024,083 A (KABLAOUI et al) 17 May 1977, col. 1, lines 52-63.	1-78
A	US 3,440,029 A (LITTLE et al) 22 April 1969, col. 1, lines 16-26.	1-78